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Miscibility of Starch and Low Molecular Weight Poly (ethyleneglycol) Blends in Aqueous Medium

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Abstract

The miscibility of starch and poly(ethyleneglycol) (PEG) blends in water were investigated by viscosity, density and refractive index studies. The physical interaction parameters like poly-solvent and blend-solvent have been calculated using viscosity and density data. Starch/PEG blends were found to be miscible in all studied ratios. The study also revealed that variation of temperature does not affect the miscibility of starch and PEG blends in the aqueous solution significantly. The miscibility occurs due to presence of hydroxyl-hydroxyl interactions in the blends. The result obtained reveals that PEG can be effectively used as gelating agent in starch solution.

Keywords: Miscibility, viscosity, polymer interaction, starch, PEG.

1. Introduction

Starch is an abundant and low cost carbohydrate consisting of branched amylopectin and linear amylase structures. The gelling and film forming property of starch as attracted its use in either as

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coating or as an additive in packaging materials. The granulation of starch in solution state is due to branched and intramolecular hydrogen bonding but, granules swell and rupture, the semi-crystalline structure is lost upon increasing temperature of solution. Therefore, forms a gelatinous matrix with increase in viscosity. However, its semi crystalline and mechanical properties do not satisfy the wide range of applications. Preparation of blends with interaction with natural or synthetic polymers will certainly improve this existing drawback of starch. The application of polymer blends is widely spread in fields like medicine, agriculture, stationeries etc due to its targeted biological, mechanical or degradation properties in comparison to the individual components. Among all the alternatives, low molecular weight poly(ethyleneglycol) (PEG) is chosen for its properties such as low toxicity, immunogenicity, biocompatible and biodegradable performance. Similar blend studies of chitosan and PEG was done by Alexeev et al. and they found that there is significant improvement in mechanical properties of chitosan upon blending with PEG [1,2].

The definition of polymer blends varies with view of compactibility and miscibility. Compactible polymers may not be miscible with each other, wherein miscibility is determined by intermolecular forces. Hence, we polymer blends are physical mixtures of structurally different polymers, [3-5]. There have been various techniques of studying the miscibility of the polymer blends [6-10]. Some of these techniques are complicated, costly and time consuming. Hence, it is desirable to identify simple, low cost and rapid techniques to study the miscibility of polymer blends. Chee [8] and Sun et al [11] have suggested a viscometric method for the study of polymer-polymer miscibility in solution.

Our previous studies on miscibility showed interaction between natural-natural [12], synthetic-synthetic [13] and synthetic-natural polymer [14] blends in non-aqueous solutions. The subject of this study is to investigate the miscibility behavior of starch and PEG blends in buffer solution [15] at 303K, 313K, and 323K. The effects on molecular interactions between poly-solvent and blend-solvent interaction parameters were determined at 303K, 313K, and 323K. With hydroxyl group in starch, which can form hydrogen bonding

with terminal -OH groups of PEG functioning as weak proton donors, therefore, leading to miscibility in starch/PEG blends.

2. Experimental part

2.1 Materials

Soluble starch, medium molecular weight from Merck and pure PEG with M_w = approx. 6,000 was purchased from SIGMA-ALDRICH.

2.2 Preparation of polymer solutions

The blends of starch/PEG of different compositions were prepared by mixing solution in doubled distilled water. The total weight of the two components in solution was always maintained at 1 g dL^{-1} . Stock solutions of individual polymers and the blends of starch/PEG of different blend compositions, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80 and 10/90 were prepared in doubled distilled water.

2.3 Viscosity

Viscosity measurements were made at 303K, 313K, and 323K, using suspended level Ubbelohde viscometer, with flow time of 94s for distilled water. Solution viscosities at different temperatures were maintained in a thermostat bath, with thermal stability ± 0.1 °C.

2.4 Density and refractive index

The densities of the solutions were measured at 303K, 313K, and 323K by specific gravity bottle. The refractive index of the blend solutions were measured using Abbe's refractometer with thermostat water circulation system at 303K, 313K, and 323K. The accuracy of the refractive index measurements was ± 0.05 %.

3. Results and discussion

3.1 Solution property studies

Viscosity of the blend solutions were measured at 303K, 313K, and 323K, for different starch/PEG blend compositions at ratios of 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80 and 10/90 along with the individual pure polymer solutions in aqueous

solution at five concentrations, namely, 0.5, 0.4, 0.3, 0.2, and 0.1, (v/v) of the blends as well as pure components.

From viscosity data, reduced viscosities of the polymer solutions have been calculated and Huggin's plots of reduced viscosities of the component polymers and their blend compositions versus concentrations at 303K, 313K, and 323K temperatures are shown in Figs. 1a-1c. Fig. 1a-1c indicates the considerable higher slope variation for all blend compositions of starch/PEG. This may be attributed to the mutual attraction of macromolecules in solution, because of increase of hydrodynamic and thermodynamic interaction. Hence, the starch/PEG is found to be miscible.

The interaction parameters of the individual polymers and their blend compositions were determined using slopes and intercepts from Fig 1a-1c and the values are given in Table 1 and 2. The slope of the curve gives the corresponding interaction parameter value, which has been evaluated on the basis of classical Huggins equation [16]. Krigbaum and Wall interaction parameter Δb of the blends [17] has been obtained from the difference between the experimental and theoretical values of the interaction parameters b_{12} and b_{12}^* . Polymer 1-polymer 2 interaction parameter Δb can be calculated as follows:

$$\frac{(\eta_{sp})_m}{C_m} = (\eta)_m + b_m C_m \quad (1)$$

Where C_m is the total concentration of polymers $C_1 + C_2$, $(\eta_{sp})_m$ is the specific viscosity and b_m represents the global interaction between all polymeric species defined by the equation,

$$b_m = w_1^2 b_{11} + 2w_1 w_2 b_{12} + w_2^2 b_{22} \quad (2)$$

where w_1 and w_2 are weight fractions of polymer 1 and polymer 2, respectively, b_{12} is the interaction parameter of the blend system that can be calculated from equation (2) and b_{11} and b_{22} are respective individual interaction parameters. The interaction parameters b_{11} , b_{22} , and b_m have been calculated from the slopes of the plot of reduced viscosity versus concentration. The interaction parameter b_{12}^* was then calculated theoretically by using equation,

$$b_{12}^* = (b_{11}b_{22})^{1/2} \quad (3)$$

The difference (Δb) calculated from the theoretical b_{12}^* from equation (3) and the experimental b_{12} with equation (2) is given as

$$\Delta b = (b_{12} - b_{12}^*) \quad (4)$$

If $\Delta b > 0$, blends are miscible; and if $\Delta b < 0$ phase separation occurs. It has been found that Δb values are positive (Table 2) for all blend compositions and at all studied temperatures. This suggests that the blends are miscible in the studied range. If η_1 and η_2 are sufficiently apart, a more effective parameter μ , defined by Chee [8], can be used to predict the compatibility. The relation is given by

$$\mu = \frac{\Delta b}{(\eta_2 - \eta_1)^2} \quad (5)$$

where η_1 and η_2 are intrinsic viscosities of pure component solutions. The blend is miscible when $\mu \geq 0$ and immiscible if $\mu < 0$. The values of μ , calculated with aforementioned expression at different temperatures for the present system have been presented in Table 1.

Sun et al [11] have suggested a new formula for the determination of polymer miscibility as follows:

$$\alpha = K_m - \frac{K_1[\eta]_1^2 w_1^2 + K_2[\eta]_2^2 w_2^2 + 2\sqrt{K_1 K_2} [\eta]_1 [\eta]_2 w_1 w_2}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2} \quad (6)$$

where, K_1 , K_2 , and K_m are the Huggins's constants for individual components 1, 2 and the blend, respectively. The long-range hydrodynamic interactions are considered while deriving this equation. They have also suggested that a blend will be miscible when $\alpha \geq 0$ and immiscible when $\alpha < 0$. The α values for the present system at various temperatures have been listed in Table 1. The computed values show that both μ and α values for the system under study are positive for all blend composition indicating that the blends are miscible. Further, we have also carried out calculations to identify the miscibility of blends based on Huggins

constant. The Huggins constant is a parameter that could also be used to express the interaction between unlike polymers [17]. Hong et al. [18] used Huggins constant parameter k_{AB} value correlated with b_{AB} as shown in the below equations for unlike polymers.

$$b_{AB} = k_{AB}[\eta]_A[\eta]_B \quad (7)$$

and

$$k_{AB} = \frac{b_m - (b_A w_A^2 + b_B w_B^2)}{2[\eta]_A [\eta]_B w_A w_B} \quad (8)$$

The factor k_{AB} , is a theoretical value derived from the geometric means of k_A and k_B as

$$k_{AB,t} = (k_A k_B)^{0.5} \quad (9)$$

The deviation from the theoretical value also provides information about the interaction between unlike polymers as shown in

$$\Delta k_{AB} = k_{AB} - k_{AB,t} \quad (10)$$

The positive Δk_{AB} value indicates that the polymer mixture in solution-state is miscible. Table 2 shows the Δk_{AB} values for our system, which are positive for all compositions indicating the miscibility of the blends at 303K, 313K, and 323K, temperature ranges.

3.2 Polymer-polymer and polymer blend-solvent interactions

The interaction parameters between polymer-polymer and polymer blend-solvent are a measure of miscibility. The polymer-polymer interaction parameters (χ_i) have been computed from Flory-Huggins theory [19] with

$$\chi_i = \left(\frac{V_i}{RT} \right) (\delta_2 - \delta_1)^2 \quad (11)$$

where δ_1 and δ_2 are the solubility parameter of component polymers, respectively, and V_i , R , and T are the molar volume of the solvent, universal gas constant, and temperature (K), respectively. The same expression has also been used for the calculation of interaction parameter between polymers in polymer blends [20, 21]. The blend-solvent interaction parameters have also been calculated according to the method adopted by Singh and Singh [22]. The solubility parameters of the blend (δ) was calculated from the additively relationship,

$$\delta = X_1\delta_1 + X_2\delta_2 \quad (12)$$

where X_1 and X_2 are the mass fractions and δ_1 and δ_2 are the solubility parameters of the component polymers in the blend system. The interaction parameters of the polymer-polymer blend systems have been presented in Table 3, whereas the blend-solvent interaction parameters are given in Table 4. From these data, we observed that the net polymer-polymer interactions were higher than those observed for blend-solvent interactions for studied blend compositions at three different temperatures. Such a difference between polymer-polymer interactions and blend-solvent interactions suggested the compatible nature of the blends in the studied range.

To confirm the miscibility behavior of the blends further, density, and refractive index values of the blend solutions have been measured at three different temperatures. The variation of the density and refractive index with the blend composition is shown in Figs. 2 and 3 respectively. The graphs show linear region. It was already established [14, 22] that the variation is linear for miscible blend and non-linear for immiscible blend. In the present case, the variation is found to be linear in all blend compositions and at 303K, 313K, and 323K, temperature variations. This observation is in confirmation with μ and a values. So the present study indicates the existence of miscibility windows in all starch content in the blend. And below this composition, there will not be much interaction between the polymer segments, which leads to immiscibility of the polymer blend. Here, the miscibility of blend may be due to some specific interaction like H-bonding between hydroxyl-hydroxyl groups of starch and PEG.

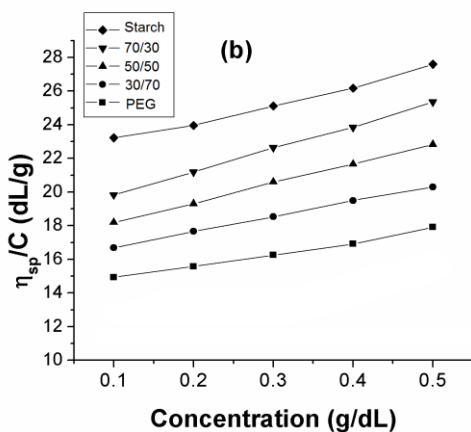
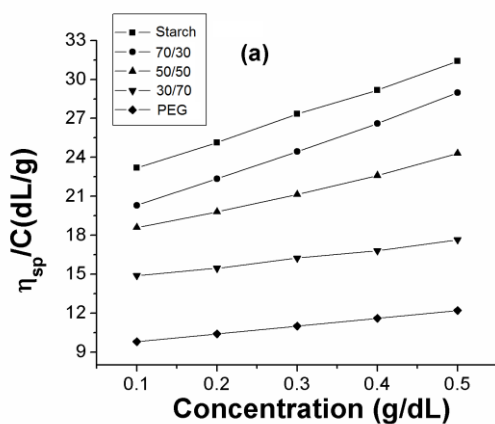
4. Conclusions

The miscibility behavior of starch and PEG blends in buffer solution has been studied in the temperature range 303K, 313K, and 323K. The miscibility has been analyzed by solution viscosity, density, and refractive index measurement of the blend solutions and calculating various interaction parameters based on these data. The μ , a , and Δk_{AB} interaction parameter test indicated that blends miscible in all temperature range studied. The results indicated the presence of positive interactions in all the blend compositions, hence, PEG can be effectively use to reduce the semicrystalline property of starch.

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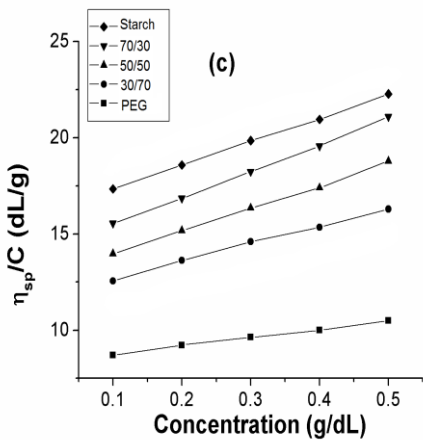


Fig 1: (a) Reduced viscosity versus concentration of starch/PEG blends at 303K, (b) Reduced viscosity versus concentration of starch /PEG blends at 313K, (c) Reduced viscosity versus concentration of starch/PEG blends at 323K.

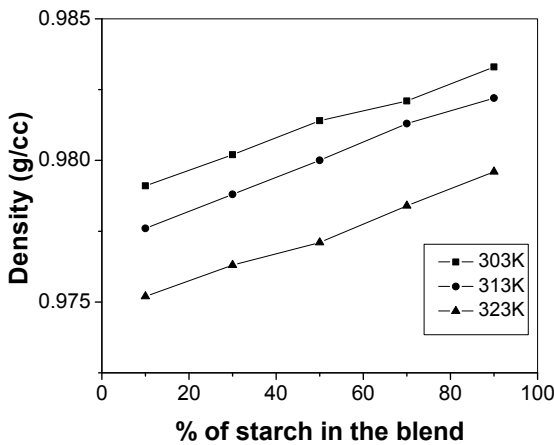
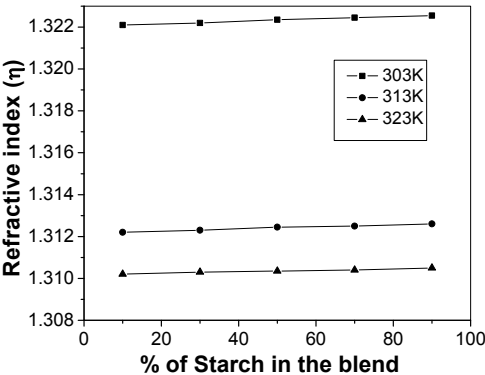


Fig 2: Variation of density of starch/PEG blend solutions with starch blend composition at different temperatures



with starch blend composition at different temperatures

Table 1: μ , and α values for the Starch/PEG Blends at Different Temperatures.

| starch/PEG (v/v) | At 303K | | At 313K | | At 323K | |
|---------------------|---------|----------|---------|----------|---------|----------|
| | μ | α | μ | α | μ | α |
| 90/10 | 0.332 | 0.287 | 0.245 | 0.231 | 0.187 | 0.154 |
| 80/20 | 0.291 | 0.249 | 0.233 | 0.224 | 0.144 | 0.121 |
| 70/30 | 0.247 | 0.218 | 0.197 | 0.185 | 0.124 | 0.113 |
| 60/40 | 0.222 | 0.205 | 0.176 | 0.172 | 0.109 | 0.101 |
| 50/50 | 0.215 | 0.193 | 0.168 | 0.157 | 0.093 | 0.087 |
| 40/60 | 0.208 | 0.184 | 0.154 | 0.144 | 0.081 | 0.071 |
| 30/70 | 0.196 | 0.166 | 0.142 | 0.132 | 0.074 | 0.058 |
| 20/80 | 0.183 | 0.151 | 0.129 | 0.126 | 0.066 | 0.047 |
| 10/90 | 0.177 | 0.142 | 0.118 | 0.115 | 0.052 | 0.035 |

Table 2: Δb and Δk_{AB} Values for the Starch/PEG Blends at Different Temperatures

| starch/PEG (v/v) | At 303K | | At 313K | | At 323K | |
|---------------------|------------|-----------------|------------|-----------------|------------|-----------------|
| | Δb | Δk_{AB} | Δb | Δk_{AB} | Δb | Δk_{AB} |
| 90/10 | 1.423 | 4.587 | 0.988 | 4.997 | 1.277 | 6.023 |
| 60/40 | 1.247 | 2.489 | 0.875 | 4.002 | 1.004 | 5.248 |
| 40/60 | 1.001 | 1.845 | 0.744 | 3.712 | 0.857 | 4.254 |
| 10/90 | 0.799 | 1.587 | 0.582 | 3.217 | 0.663 | 3.781 |

Table 3: Polymer-Polymer Interaction Parameters for the Starch and PEG in the Blend.

| Temperature (K) | Polymer | χ_i calculated from eq. (11) |
|-----------------|---------|-----------------------------------|
| 303 | starch | 0.047 |
| | PEG | 1.547 |
| 313 | starch | 0.024 |
| | PEG | 1.471 |
| 323 | starch | 0.017 |
| | PEG | 1.280 |

Table 4: Blend-Solvent Interaction Parameters at Different Temperatures.

| Temperature (K) | starch/ PEG (v/v) | δ calculated from eq. (12) | χ_i calculated from eq. (11) |
|-----------------|----------------------|--------------------------------------|--------------------------------------|
| 303 | 10/90 | 2.569 | 0.0074 |
| | 40/60 | 2.621 | 0.0071 |
| | 60/40 | 2.714 | 0.0203 |
| | 90/10 | 2.817 | 0.0427 |
| 313 | 10/90 | 2.485 | 0.0065 |
| | 40/60 | 2.522 | 0.0068 |
| | 60/40 | 2.658 | 0.0111 |
| | 90/10 | 2.777 | 0.0127 |
| 323 | 10/90 | 2.321 | 0.0057 |
| | 40/60 | 2.310 | 0.0069 |
| | 60/40 | 2.277 | 0.0103 |
| | 90/10 | 2.263 | 0.0114 |